Dispersion stability and anti-oxidation of an aqueous Zirconium Diboride slurry with a high solid loading

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In this paper, the dispersion stability of zirconium diboride (ZrB_2) slurries and their anti-oxidation behavior to prevent re-oxidation in the ZrB_2 slurries were studied.

SPEX-milled ZrB_2 powder was used to improve the dispersion stability, and the viscosity and zeta potential as a function of pH were measured in order to confirm the dispersion behavior in aqueous ZrB_2 slurries using various additives [polyethylenimine (PEI), polyacrylic acid (PAA), polyvinyl pyrrolidone (PVP), and polyvinyl alcohol (PVA)]. In addition, the oxygen contents were measured before and after processing to evaluate the oxidation behavior in the ZrB_2 slurries.

By using 2 wt % PEI, the isoelectric point (IEP) of the ZrB_2 slurry increased from a pH of 5.8 to above a pH of 12. Also, the viscosity was below 6.27 mPa·s in the 20 vol % ZrB_2 slurry at pH values of 2–12. The oxygen content of the ZrB_2 powders increased from 2.42 to 3.79 wt % after preparing an aqueous slurry, but by using 2 wt % PVP and 2 wt % PEI, the oxygen contents of the 20 vol % ZrB_2 slurry could be reduced from 3.79 to 2.6 and 2.8 wt %, respectively. Consequently, a 50 vol % ZrB_2 slurry with an oxygen content was 2.92 wt % could be prepared in the pH range of 6–9 using 2 wt % PEI.

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1. Introduction

Ultra High Temperature Ceramics (UHTCs) have been a main subject of recent research in the field of structural ceramics. Among the UHTCs, ZrB_2 has a high melting point above 3,200°C, a Young's modulus of about 500 GPa, a hardness of 23 GPa, a chemically stable crystal structure, high electrical and thermal conductivities, and good resistance for corrosion. Because of these properties, ZrB_2 has been used for refractory and structural materials such as refractory linings, electrodes, micro-electronic technology applications, and cutting tools. ZrB_2 has also been considered as a promising candidate for aerospace materials such as hypersonic aircraft, atmosphere re-entry spacecraft, and rocket propellants.^{1),2)}

However, in order to apply this material in usable components, the fabrication of ZrB_2 structures with complex geometries is required. A pressureless sintering process including a colloidal process is suitable for manufacturing ZrB_2 structures with complex geometries. In addition, complex geometries could be manufactured by using colloidal processing such as slip casting, tape casting, and injection molding. Dispersion stability and a high solid loading in slurries are essential during the colloidal process. Therefore, additives have been used to increase the dispersion stability and mechanical treatment has been applied to decrease the particle size.³⁾

Many researchers have been investigated the dispersion stability of ZrB_2 slurries using various additives.^{3)–8)} Generally, the mechanism for enhancing the dispersion stability by using additives can be divided into four categories. First, in electrostatic stabilization, the dispersion effect is improved due to repulsive forces between like charges. There is an energy barrier large

enough to overcome the attractive van der Waals forces between the particles. Second, steric stabilization may be present such that particles cannot approach each other due to the adsorption of organic polymer on the surfaces of particles. Third, electro-steric stabilization is a combination of electrostatic stabilization and steric stabilization. Finally, controlling the dispersion and agglomeration by macromolecules between the particles and not absorbed on the surfaces of particles is referred to as depletion stabilization.⁹⁾ In this study, four different additives were used and their properties are summarized in **Table 1**.

ZrB_2 has a low intrinsic sinterability due to its strong covalent bonding, low self-diffusion coefficient, and surface oxide impurities. In particular, oxide impurities on the surface of ZrB_2 powder such as ZrO_2 or B_2O_3 interrupt densification. The oxide impurities lead to low bulk and grain boundary diffusion rates. In addition, the oxide impurities supply a rapid diffusion passage to accelerate coarsening. During the grain coarsening, the surface area of the particles decreases reducing the driving force for densification.^{10)–12)} Oxide impurities are formed by oxidation reactions with H_2O or alcohol in the solvent.^{13),14)} It is considered that the oxidation reactions can be prevented by coating a polymer layer on the surface of the powder using additives.

In this study, we investigated the dispersion stability and anti-oxidation behavior in aqueous ZrB_2 slurries using various additives (PEI, PAA, PVP, and PVA) and discuss their mechanisms.

2. Experimental procedure

ZrB_2 (Grade: $\text{ZrB}_2\text{-F}$, Japan New Metals Co., Osaka, Japan) powder with an average particle size of 2.42 μm and an oxygen content of 1.23 wt % was used as the starting material. PEI (Sigma Aldrich Corp., St. Louis, MO, USA; molecular weight (MW): 10,000), PAA (Sigma Aldrich Corp., St. Louis, MO, USA; molecular weight (MW): ~1,800), PVP (Sigma Aldrich Corp., St. Louis, MO, USA; molecular weight (MW): 40,000),

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Table 1. Characteristics of the various additives

	PEI	PAA	PVP	PVA
Structural formula
Solubility in water	soluble in hot water	good	good	good
The type of dispersion stabilization	electrostatic stabilization	electrostatic stabilization	steric or/and depletion stabilization	steric stabilization

Table 2. ZrB₂ slurries produced under various conditions

Solid loading (vol %)	Type of additives	Amount of additive (wt %)
20	PEI	2
	PVA	
	PVP	
	PAA	
20	PEI	0.5
		1
		2
		3
		4
		5
30	PEI	2
40		
45		
50		

and PVA (Sigma Aldrich Corp., St. Louis, MO, USA; molecular weight (MW): 89,000–98,000) were used as additives. ZrB₂ powders were pulverized by a SPEX mill (model 8000D, Spex-Certiprep Inc., Metuchen, NJ, USA) for 6 h using a WC jar and media. The particle size of the ZrB₂ powder was measured by a particle size analyzer (LA-950V2, HORIBA Ltd., Kyoto, Japan) before and after milling.

The batch conditions including the additives, compositions, and the solid loading amounts are shown in **Table 2**. The ZrB₂ powder and additives were mixed in DI water and stirred for 24 h. The viscosity and zeta potential as a function of pH of the stirred slurries were measured by a rheometer (Thermo SCIENTIFIC HAAKE MARSIII, MCIK, Seoul, Korea) and a zeta potential analyzer (ELSZ, Otsuka Electronics Co., LTD, Japan), respectively, where diluted HCl and NaOH solutions were used for the titration. Before and after colloidal processing, the oxygen contents of the ZrB₂ powders were measured by using the combustion gas hot extraction method (Model TC-600, LECO Co., St. Joseph, MI, USA) in order to confirm the oxidation behavior of the ZrB₂ slurries.

3. Results and discussion

The particle size distributions of the as-received and SPEX-milled ZrB₂ powders are shown in **Fig. 1**. In **Fig. 1**, both the as-received and milled ZrB₂ powders have mono particle size distributions where the milled powder is more pronounced in the fine area than the as-received powder. The average particle sizes of the as-received and milled powders were 2.42 and 0.51 μm , respectively, demonstrating that the particle size decreased significantly after milling.

The oxygen contents of the as-received ZrB₂ powder increased from 1.23 to 2.41 wt% after milling. It is considered that the acceleration of the oxidation reaction resulted from heat gen-

Fig. 1. (Color online) Particle size distributions of as-received and SPEX-milled ZrB₂ powders.

Fig. 2. Scanning electron microscope images of the (a) as-received and (b) SPEX-milled powders.

erated by collisions between the WC jar and media and increased surface area resulting from the decreased particle size after SPEX milling.

Figure 2 shows the powder morphologies of the as-received and SPEX-milled ZrB₂ powders. Most of the particles have a spherical shape and the particle size decreased significantly after milling. It is considered that the decreased particle size due to the milling process is effective to increase the dispersion stability by decreasing gravity effects. The behavior can be confirmed by Eq. (1).

$$V_s = g(\rho_s - \rho_l)d^2/18\eta \quad (1)$$

Here, V_s is the Stokes velocity, g is the acceleration of gravity, ρ_s is the density of the solid particles, ρ_l is the liquid density, d is the size of a single particle, and η is the fluid viscosity.¹⁵⁾

Figure 3 shows the viscosity as a function of the pH in the ZrB₂ slurry with the various additives. With PVP and PVA, the viscosity changed significantly as a function of pH and it was relatively higher than the viscosities with the other additives. On

Fig. 3. (Color online) Viscosity of the 20 vol% ZrB₂ slurries containing 2 wt % of the various additives.

Fig. 4. (Color online) Zeta potential of the ZrB₂ slurries containing 2 wt % of the various additives.

the other hand, the ZrB₂ slurry with PEI was the most stable because it had a low viscosity in the overall pH range. The ZrB₂ slurry with PAA is also stable with a low viscosity of less than 6.27 mPa·s in the pH range of 4–10.

Also, the viscosities of the ZrB₂ slurry with PEI or PAA were lower than those of the slurry without an additive. Generally, the viscosity decreases along with an improvement of the dispersion stability.^{3),16),17)} Therefore, it is considered that the lower viscosity is due to electrostatic stabilization by PEI and PAA. These results demonstrate that PEI and PAA are more effective additives for dispersion in the ZrB₂ slurries.

The zeta potentials as a function of pH with the four additives are shown in Fig. 4. The zeta potential represents the amount of charge on the surface of the particles in the slurry. A high absolute value of the zeta potential indicates effective dispersion due to strong repulsion between particles.

In Fig. 4, PEI and PAA are the most effective additives for dispersion. By using PAA and PEI, the isoelectric point (IEP) of the ZrB₂ slurry shifted from a pH of 5.8 to a pH of 2.75 and a pH above 12. The absolute values of the zeta potential in the ZrB₂ slurries with PEI and PAA are the highest above a pH of 5 and below a pH of 9, respectively. These highest absolute values of the zeta potential may be effective for dispersion due to the strong repulsion between particles.

Fig. 5. (Color online) Oxygen contents of the ZrB₂ in 20 vol% ZrB₂ slurries containing 2 wt % of the various additives.

Table 3. Effects of the additives on the dispersion stability, viscosity, and anti-oxidation behavior of the slurries

	PEI	PAA	PVP	PVA
Dispersion stability	○	○	△	×
Viscosity	low	low	middle	high
Anti-oxidation	○	△	○	×

○: Good, △: Normal, ×: Bad.

On the other hand, the absolute values of the zeta potential in the ZrB₂ slurry with PVP and PVA are lower than those in the slurry without an additive. These results showed the same trend of the above mentioned viscosity data shown in Fig. 3.

In this study, the dispersion stability in the ZrB₂ slurry and the anti-oxidation behavior of the ZrB₂ powder in the slurry were studied. Tieshu Huang et al. reported that the pH does not have a significant effect on the oxidation rate in ZrB₂ slurries.³⁾ Therefore, the experiments were carried out at a fixed pH of 7. The oxygen contents of the ZrB₂ powders in the slurries with the four additives are shown in Fig. 5. The oxygen content of the milled ZrB₂ powders increased from 2.41 to 3.79 wt% during the colloidal process. It is considered that the oxygen contents increased by the oxidation reaction with the water used as the solvent.

Also, the oxygen contents of the ZrB₂ powders in the slurries with the different additives except for PVA were lower than that of the powder in the slurry without an additive. It is considered that the oxidation reaction was prevented by a polymer coating layer on the surface of the ZrB₂ particles. On the other hand, the oxygen content in the slurry with PVA was higher than that without an additive. In addition, it is considered that the oxidation reaction occurred due to the OH functional groups of PVA. Among the three effective additives for anti-oxidation, the oxygen content of the ZrB₂ powder in the slurry with PVP was the lowest at 2.60 wt%, but the dispersion stability was not good, as shown in Figs. 3 and 4. The ZrB₂ slurries with PAA or PEI have good dispersion stabilities but the oxygen contents are 3.53 and 2.80 wt %, respectively. As a result, PEI is a more effective additive for anti-oxidation. From these results, PEI is the most effective additive which simultaneously improves the dispersion stability and anti-oxidation properties, as summarized in Table 3.

Fig. 6. (Color online) Viscosity of the 20 vol% ZrB₂ slurry as a function of the PEI content.

Fig. 7. (Color online) Zeta potential of the ZrB₂ slurry as a function of the PEI content.

The viscosity as a function of the amount of PEI in the ZrB₂ slurry is shown in Fig. 6. The viscosity decreased with increasing PEI content up to 2 wt % but then increased above 3 wt %. When two surfaces covered by a macromolecule approach each other, steric repulsion is activated due to the polymer coating. However, it is also possible that the same polymer molecule may absorb to more than one particle at the same time, thereby forming a link between particles. This phenomenon is called bridging flocculation and produces an unstable slurry.¹⁸⁾ It is considered that the viscosity of the ZrB₂ slurries with more than 3 wt % PEI increased by this bridging flocculation. Therefore, the slurry with 2 wt % PEI, which had the lowest viscosity, is the optimum condition for dispersion.

Figure 7 shows the zeta potential of ZrB₂ as a function of the PEI content. The zeta potential increased with the addition of PEI and the zeta potential of the slurry with over 1 wt % PEI maintained a high value in the pH range of 2–9. It can be found that ZrB₂ particles in the slurry were stably charged on the surface in the pH range of 2–9.

In Figs. 6 and 7, the absolute values of the zeta potentials of the slurries with over 1 wt % PEI were very similar, but the viscosity was the lowest in the slurry with 2 wt % PEI. Therefore, it is considered that the addition of 2 wt % PEI is optimal for dispersion stability.

Fig. 8. (Color online) Viscosity of the ZrB₂ slurry as a function of the solid loading contents with 2 wt % PEI.

The viscosities of the slurries with 2 wt % PEI as a function of the solid loading are shown in Fig. 8. The viscosity increased with increasing solid loading amount from 20 to 50 vol %. We were able to fabricate ZrB₂ slurries with a high solid loading of up to 50 vol % in the pH range of 6–9 with an oxygen content of 2.92 wt %. The viscosity of the slurries with solid loadings over 50 vol % could not be measured and the dispersion could not be maintained because of sedimentation. Also, the viscosities in the slurries with solid loadings of 20 and 30 vol % maintained similar low values. The viscosity of the slurry with solid loadings over 40 vol % significantly increased with increasing solid loading.

Therefore, it is considered that the addition of 2 wt % PEI is the most effective for dispersion stability and anti-oxidation in the ZrB₂ slurry.

4. Conclusions

In this study, the dispersion stability of ZrB₂ slurries and anti-oxidation behavior for preventing re-oxidation in the ZrB₂ slurries using additives (PEI, PAA, PVP, and PVA) were studied. The viscosity and zeta potential were measured to determine the most effective additive for dispersion stability. The viscosities in the slurries with PEI and PAA were lower than with the other additives because of the stability resulting from electrostatic stabilization. The zeta potential values also showed the same tendency.

The oxygen contents of the ZrB₂ powders were measured to determine the most effective additive for anti-oxidation. By using 2 wt % PEI and 2 wt % PVP, the oxygen contents of the milled ZrB₂ powders decreased from 3.79 to 2.80 and 2.60 wt %, respectively. It is considered that the oxidation reaction was prevented by a polymer coating layer on the surface of the ZrB₂ particles. From these results, PEI is the most effective additive which simultaneously provides dispersion stability and anti-oxidation characteristics.

For the PEI additive, the viscosity and zeta potential were measured to understand the dispersion stability as a function of the amount of PEI. As a result, 2 wt % PEI was the optimal condition for dispersion stability.

As a result, by using 2 wt % PEI, the 50 vol % solid loading ZrB₂ slurry could be prepared in the pH range of 6–9 and its oxygen content was 2.92 wt %.

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